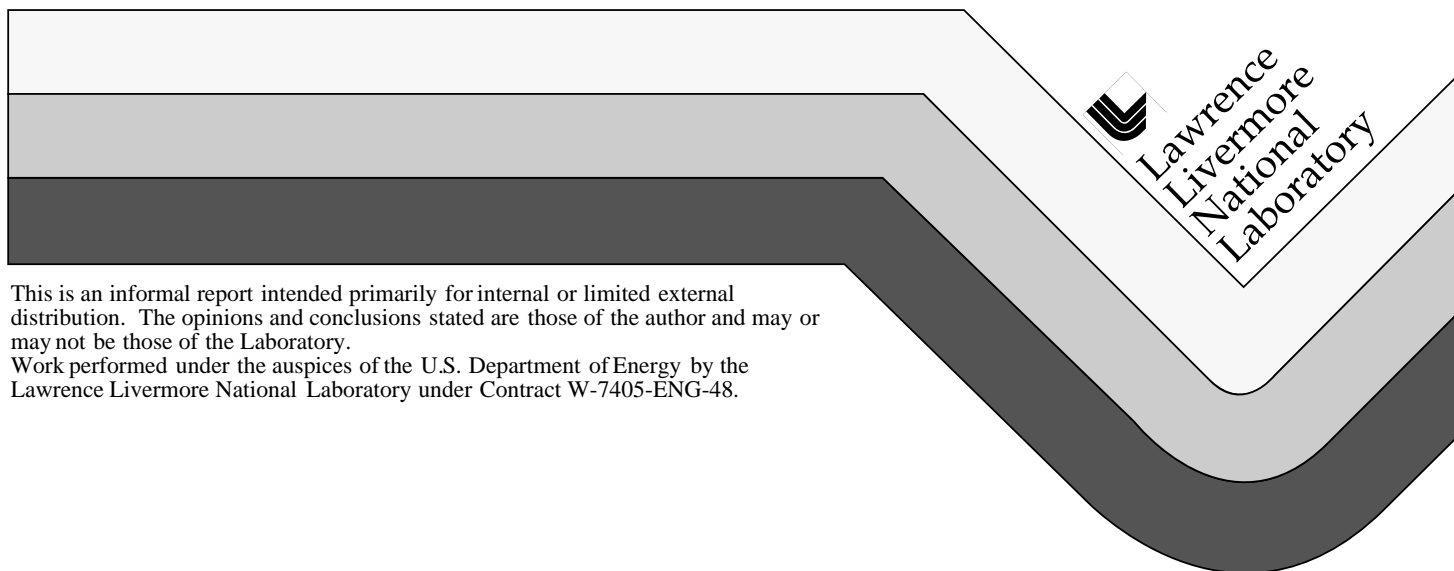


MSO Spent Salt Clean-Up/Recovery Process

P.C. Hsu
L.J. Summers
E.H. von Holtz
W.A. Brummond
F.T. Wang
M.G. Adamson

February 1, 1997



DISCLAIMER

This document was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor the University of California nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or the University of California, and shall not be used for advertising or product endorsement purposes.

This report has been reproduced
directly from the best available copy.

Available to DOE and DOE contractors from the
Office of Scientific and Technical Information
P.O. Box 62, Oak Ridge, TN 37831
Prices available from (423) 576-8401

Available to the public from the
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Rd.,
Springfield, VA 22161

MSO Spent Salt Clean-Up/Recovery Process *

Peter C. Hsu, Leslie Summers, Erica von Holtz,
David Hipple, William Brummond,
Francis Wang, and Martyn Adamson

Lawrence Livermore National Laboratory
P.O. Box 808
Livermore, CA 94551-0808

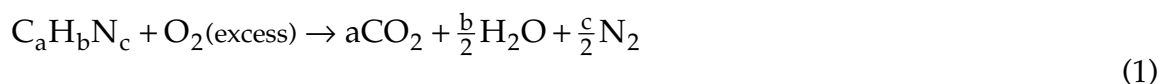
Abstract

An effective process has been developed to separate metals, mineral residues, and radionuclides from spent salt, a secondary waste generated by Molten Salt Oxidation (MSO). This process includes salt dissolution, pH adjustment, chemical reduction and/or sulfiding, filtration, ion exchange, and drying. The process uses dithionite to reduce soluble chromate and/or sulfiding agent to suppress solubilities of metal compounds in water. This process is capable of reducing the secondary waste to less than 5% of its original weight. It is a low temperature, aqueous process and has been demonstrated in the laboratory [1].

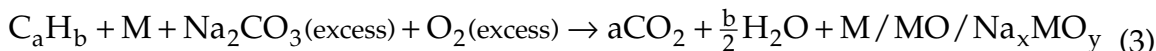
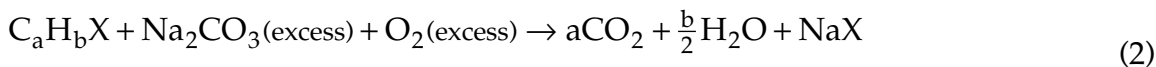
Introduction

Molten Salt Oxidation (MSO) is a thermal process that has the inherent capability of completely destroying organic constituents of mixed wastes, hazardous wastes, and energetic materials [2,3]. MSO is ideally suited to the destruction of organic waste in the form of gases, liquids, slurries, sludges, and solids on the order of 6 mm or less [4].

The MSO system consists of a reactor vessel, off-gas treatment, and salt separation process. In our current design, the reactor contains a turbulent bed of molten sodium carbonate which is used as a heat transfer and reaction medium. Oxidant air is injected into the salt bath along with the waste stream. The waste reacts, converting organic components of the waste into carbon dioxide, nitrogen, and water. Elements like halogens and sulfur, which would otherwise be converted into acid gases, are "scrubbed" and trapped in the salt in forms such as sodium chloride and sodium sulfate. Radionuclides, metals and other non-oxidizable inorganic constituents that may be in the waste form are captured and held in the salt bath for future disposal. Equations 1-3 provide generic examples of principal reactions [4]:



*This work was performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore National Laboratory under contract number W-7405-ENG-48.



where X represents halogens and M represents metals.

Spent Salt Clean-Up/Recovery Process

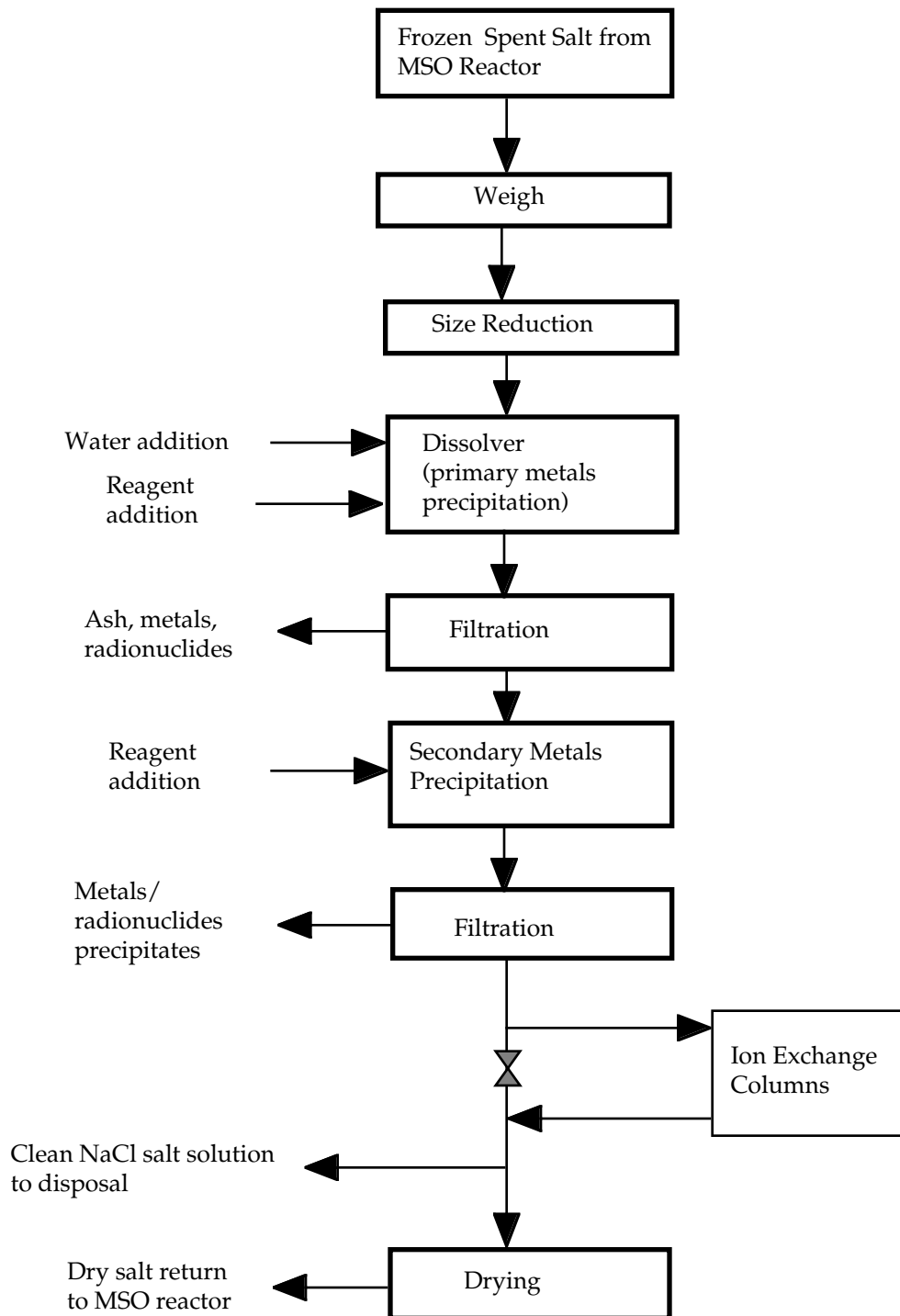
As the MSO system continues to run, inorganic products resulting from the reaction of halides, sulfides, phosphates, metals, etc., with carbonate build up in the salt bath. These must be removed to prevent complete conversion of the sodium carbonate, which would result in eventual losses of destruction efficiency and acid scrubbing capability. When the MSO reactor is used to oxidize combustible solids, "ash" (e.g. mineral residues such as Al_2O_3 and SiO_2) will build up in the salt melt and increase the viscosity of the melt. High viscosity will affect destruction efficiency; at this point the salt must be withdrawn and the ash removed.

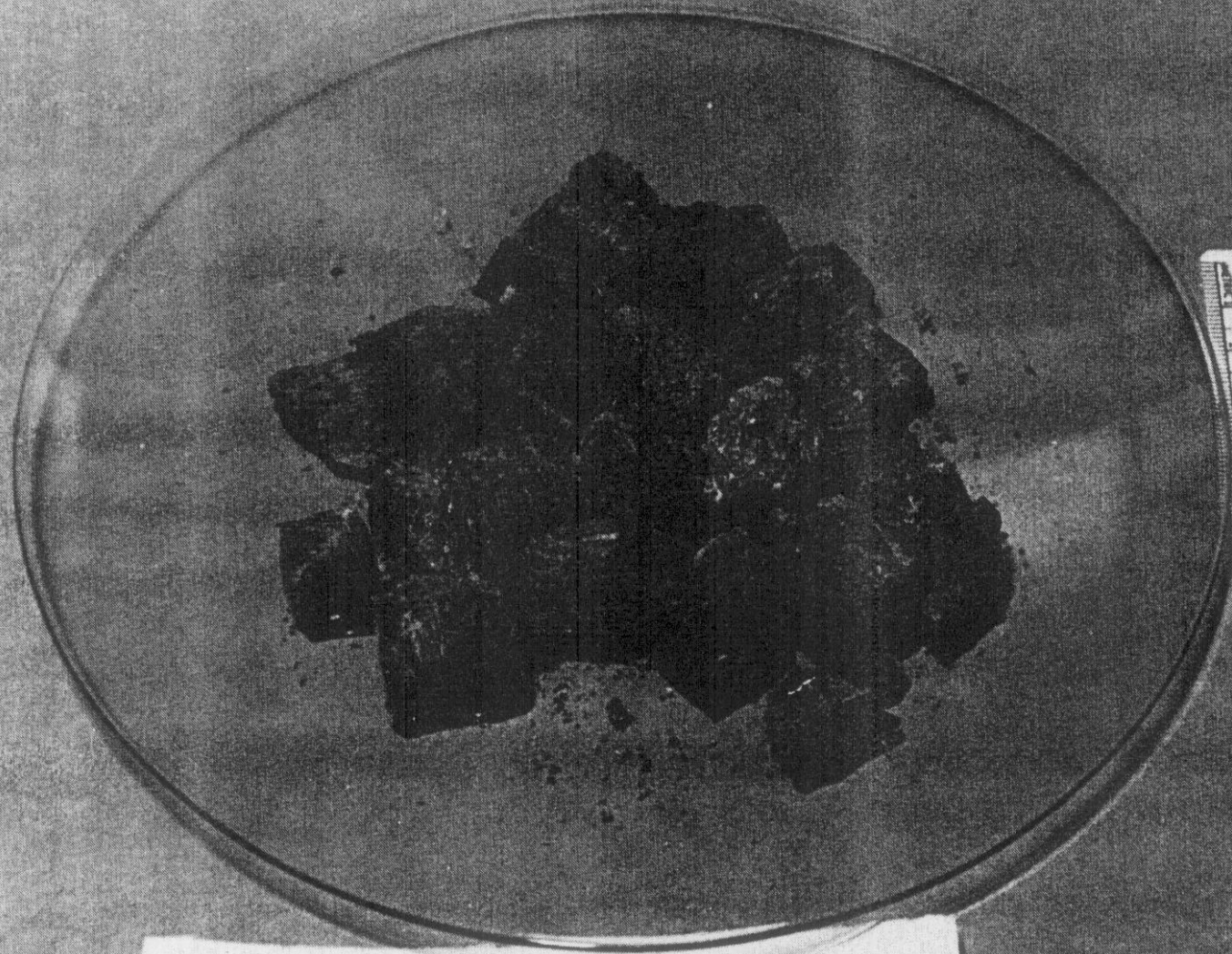
There are two operational modes for salt removal: (1) during reactor operation a slip-stream of salt melt is continuously withdrawn with continuous replacement by carbonate, or (2) the spent salt melt is discharged completely and the reactor then refilled with carbonate in batch mode. Because many of the metals and/or radionuclides captured in the salt are hazardous and/or radioactive, without further treatment the removed spent salt would create a large secondary waste stream. A spent salt clean-up/recovery system will segregate these materials and minimize the amount of secondary waste. These materials can then be encapsulated for final disposal.

Figure 1 shows the block flow diagram of spent salt cleanup/recovery system. Salt melt withdrawn from MSO reactor is frozen and cooled to ambient temperature. Depending the type of salt freezer used, further size reduction is generally required to reduce the size of spent salt particles to about 6 -12 mm before processing the salt in the salt clean-up step. Small spent salt particles are preferred to reduce the dissolution time; Table 1 shows salt dissolution time in room temperature water as a function of particle size. Salt used in this study contained 10 mole% sodium chloride and 90 mole% sodium carbonate, dissolved in 30% excess water while mixing at 400 rpm.

Figure 2 is a picture of the spent salt used with an average particle size of about 12 mm. From the data in Table 1, about 30 minutes would be needed to dissolve this spent salt.

Figure 1: Flowsheet for Aqueous Processing of Spent Salt



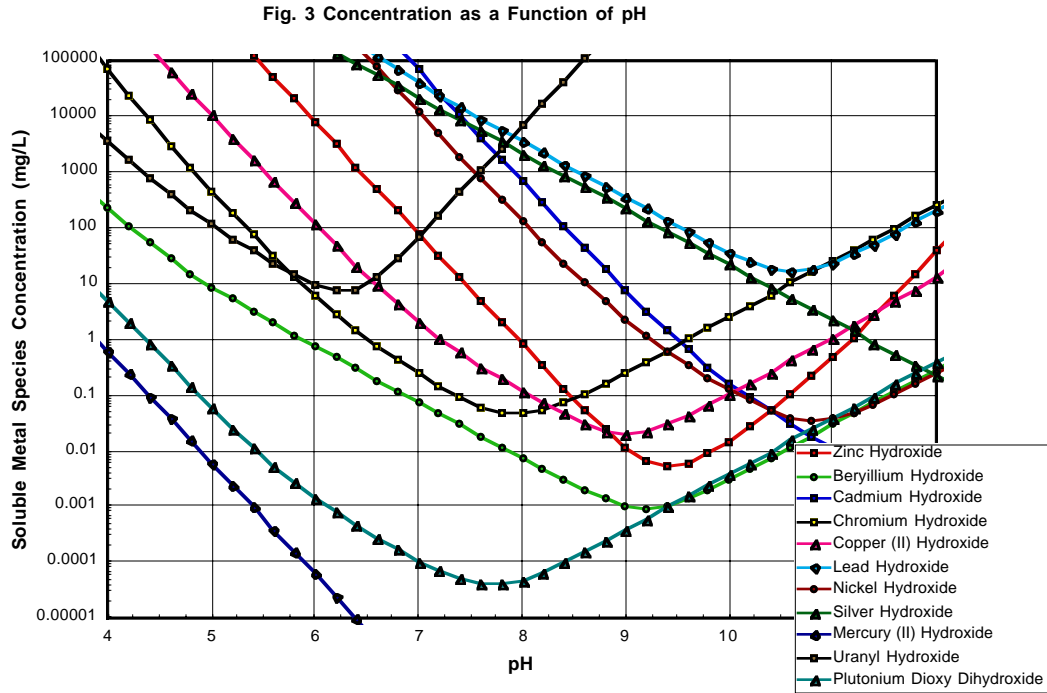


Spent Salt

Figure 2

Table 1: Dissolution Time of High Carbonate Spent Salt in Room Temperature Water

Particle size	Dissolution time
≤ 1.2 mm	< 15 minutes
1.2 - 3.3 mm	< 15 minutes
3.3 - 5.6 mm	< 15 minutes
≥ 5.6 mm	< 30 minutes



Most of mineral residues in the spent salt have low solubilities in water, depending on solution pH values, and will precipitate as metal oxides and metal hydroxides during the dissolution step. Figure 3 shows solubilities of several metal species in water at room temperature [5]. Although solubilities vary greatly with solution pH values, most metal species are less soluble in alkaline solutions. Table 2 shows optimum pH value that will minimize the solubility for each metal species in the solution. Therefore, it is desirable to maintain the solution pH values in the dissolver above 8 to minimize the concentrations of soluble metal species in the solution.

Table 2: pH Values for Minimum Solubility [5]

Metal species	pH at minimum solubility
Beryllium	9.2
Cadmium	11.6
Chromium (Cr ³⁺)	8.0
Copper	9.0
Lead	10.6
Mercury	14.0
Nickel	10.8
Plutonium	7.8
Silver	14.0
Uranium	6.2
Zinc	9.4

Most of metal sulfides have much lower solubilities than metal oxides and hydroxides in water. In order to further suppress the concentrations of metal species in the solution, sulfiding the solution with certain reagents may be needed. An aqueous process modeling code, EQ3/6, developed by Wolery [6], was used to simulate the sulfiding process for a spent salt solution containing ions of carbonate, chloride, zinc, nickel, chromate, copper, cobalt, arsenic, and silver. Sodium hydrogen sulfide, NaSH, was used as the sulfiding agent. Table 3 shows that the concentrations of metal ions in the salt solution after the sulfiding process are reduced by several orders of magnitude. During such a process, however, care must be taken in equipment design to properly vent the emission of H₂S, a by-product of the sulfiding reaction.

Table 3: Effect of Sulfiding

Metal	Concentration of ions in solution*, ppm	
	Before sulfiding	After sulfiding
As	12.7	4.5x10 ⁻⁴
Cr	177.0	6.8x10 ⁻⁹
Co	6.4	9.9x10 ⁻⁵
Cu	0.86	3.5x10 ⁻¹³
Ni	6.6x10 ⁻³	1.9x10 ⁻¹²
Ag	2.57	1.1x10 ⁻¹³
Zn	1.9x10 ⁻⁴	4.3x10 ⁻¹⁴

* at room temperature with solution pH value at 11 [7]

Addition of other reagents may be required in separate steps to convert the valence state of dissolved metals into insoluble forms. For example, use of dithionite in the secondary metals precipitation step reduces soluble Cr^{6+} to Cr^{3+} , with subsequent formation of the insoluble species $\text{Cr}(\text{OH})_3/\text{Cr}_2\text{O}_3$. Solubilities of chromium hydroxide and chromium oxide vary with pH, but are very low in alkaline solutions.

As the metals come out of solution in all stages, they tend to form submicron size particles. Reagents such as Alum [$\text{Al}_2(\text{SO}_4)_3$] can be very effective in facilitating the coagulation & precipitation process to avoid an excessive holding time in the dissolver tank. The addition of coagulant aids such as activated silica will enhance coagulation by promoting the growth of large, rapid-settling flocs. Activated silica is a short-chain polymer that serves to bind together particles of microfine aluminum hydrate. Table 4 shows that alum and activated silica reduce the time required for the start of precipitation from 85 minutes to 25 minutes for a spent salt containing 20% NaCl, 78.8% Na_2CO_3 , and 0.2% Na_2CrO_4 dissolved in water with 1% dithionite added for the chrome reduction.

Table 4: Time Required for Precipitation is Reduced With Addition of Alum and Activated Silica

Run ID	Coagulant $\text{Al}_2(\text{SO}_4)_3$ g/100 mL soln	Coagulant aid SiO_2 g/100 mL soln	Time, minutes
S	0	0	85
C1 0.015	0.001	75	
C2 0.15	0.01	25	

Filtration of the salt solution occurs after initial dissolution, for “ash”/mineral residue removal, and after addition of reagents to further remove dissolved metal species. Selection of an appropriate filter element is crucial for complete capture of suspended solid particles. The pore size of the filter element should be one micron or less for high capture efficiency.

After the secondary metals precipitation and subsequent filtration, the salt solution is very clean and contains mostly carbonate with low halides content and very low metals content. The solution can then be dried and reused.

If the waste feed to MSO reactor is halogen-rich, sodium carbonate is essentially all converted to various sodium halides. When less than 10% of the salt melt is sodium carbonate, the melt’s acid gas scrubbing capability and oxidation efficiency drop significantly, and the melt needs to be withdrawn

and replaced. Because of its low carbonate content, heating the dissolver or using warm water for salt dissolution will facilitate the process. Processing of the high-halide spent salt is similar to that of high-ash spent salt with the exception that the salt solution may be a weak alkaline solution or weak acidic solution. Solution pH values need to be carefully adjusted to improve removal efficiencies of metal species; addition of NaOH or HCl may be used if necessary. After the secondary metals precipitation and the subsequent filtration, the salt solution contains mostly halides with low carbonate content and very low metals content which can be discharged to disposal facility.

If the MSO reactor oxidizes waste feed which contains radionuclides, the radionuclides will be captured and held in the salt. Most radioactive compounds would co-precipitate with ash/mineral residue and will be removed from the salt solution after the dissolution and first filtration step. Some radionuclides, such as thorium and uranium, may form complex ions and stay in the solution. For example, predictions using EQ 3/6 indicate on the order of 300 ppm of uranium, as $\text{UO}_2(\text{CO}_3)_3^{4-}$, would remain in carbonate solution [7]. However, most uranium can be removed in the secondary metals precipitation step by adding complex ion breakers and/or reducing agents [8]. An ion exchange column is also needed to further removed radionuclides from the solution. A variety of commercial ion exchange resins are available; selection of the best resin will be done based on radionuclide content of the waste [9].

EDU Spent Salt Clean-Up Experiment and Results

LLNL built an engineering development unit (EDU, a MSO reactor) in 1995 with salt bed capacity of up to 100 kg. It has been run for several hundred hours using various feed materials, including chlorinated hydrocarbons, with good results. The chloride content in the salt bed of EDU was brought to > 90 wt% as a result of oxidizing chlorinated organic liquids. The spent salt from EDU served as an excellent source of material for developing and demonstrating an efficient spent salt clean-up process.

1. Salt Freezing, Grinding, and Analysis

The EDU salt melt was removed from the reactor after being used for six months, and was frozen into large pieces, several kilograms in size. These large pieces were then hammered and ground into salt particles smaller than 12 mm. X-ray Fluorescence (XRF) was used to determine the elemental composition of spent salt, which is shown in Table 5.

Table 5: Elemental Composition of EDU Spent Salt

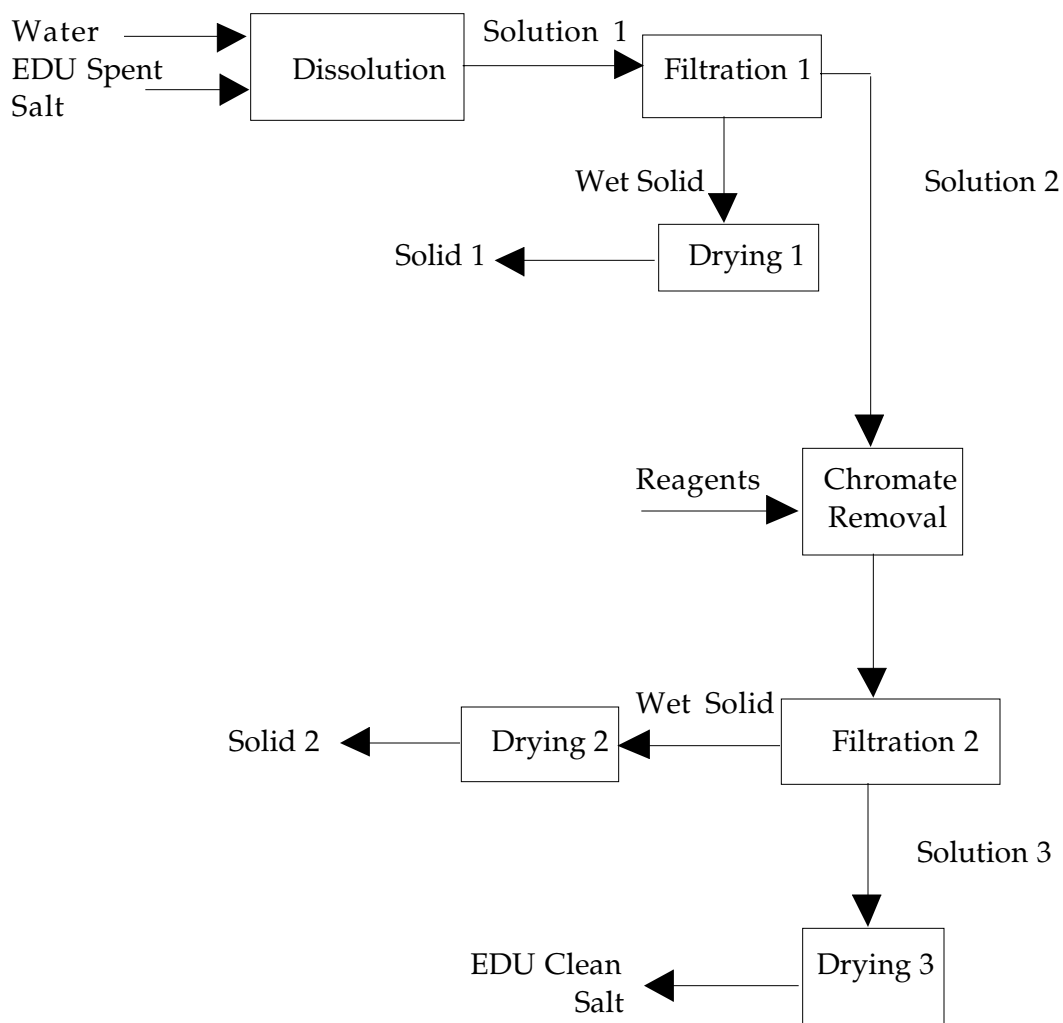
Element	Composition, wt%	Element	Composition, wt%
C	0.99	O	1.98
Na	38.69	Si	0.04
P	0.01	S	0.08
Cl	57.54	K	0.01
V	0.014	Cr	0.48
Mn	0.03	Fe	0.04
Ni	0.04	Cu	0.03
Br	0.00	Mo	0.02
Pt	0.01		

Table 5 indicates that the spent salt contains about 95 wt% sodium chloride along with minor amounts of several metals. The metallic elements in the spent salt are mostly from the corrosion of the Inconel 600 reactor and internal components such as stainless steel baffles. Although the percentage of metals in the spent salt is only about 1 wt%, it can be further reduced by using Inconel as the construction materials for internal components. Many of the metals present are at levels exceeding the RCRA land-ban criteria and this salt would be considered a hazardous waste if disposed of without further clean-up.

2. Dissolution of Spent Salt

Figure 4 depicts the flowsheet for the lab-scale clean-up experiment. Four hundred grams of ground spent salt was dissolved into 1500 mL of ambient deionized water with agitation in a 2 L glass beaker. The dissolution took less than 30 minutes, with no appreciable temperature rise – an indication of very low carbonate content in the spent salt. The solution was dark in color, with suspended particles of metal hydroxides and metal oxides (Figure 5, left). The solution was slightly acidic (pH value of 6.2), probably due to the presence of metal ions. A portable colorimeter, along with several analytical kits which are inexpensive, fast, and fairly accurate, were used to analyze ion concentrations in the solution. Formation, coagulation, and precipitation of metal hydroxides/metal oxides may be slow; consequently, soluble metal ion concentrations may vary with time. Solution analysis should be done before deciding whether sulfiding is required. To establish a baseline, no initial sulfiding was done while the solution was allowed to settle for 40 hours before filtration. The solution was analyzed at 1 hour, 22 hours and 40 hours; the results are shown in Table 6.

Figure 4: Flowsheet for EDU Spent Salt Cleaning



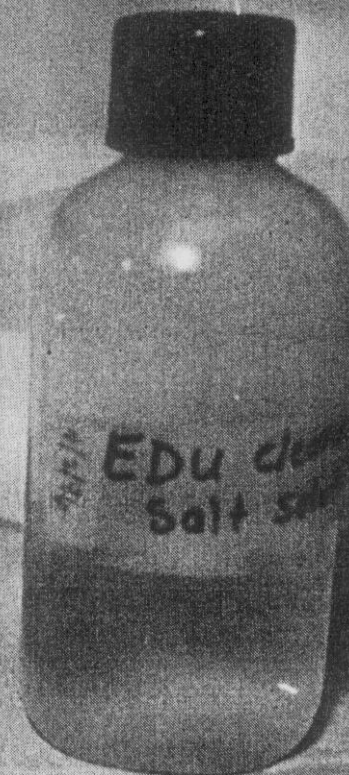
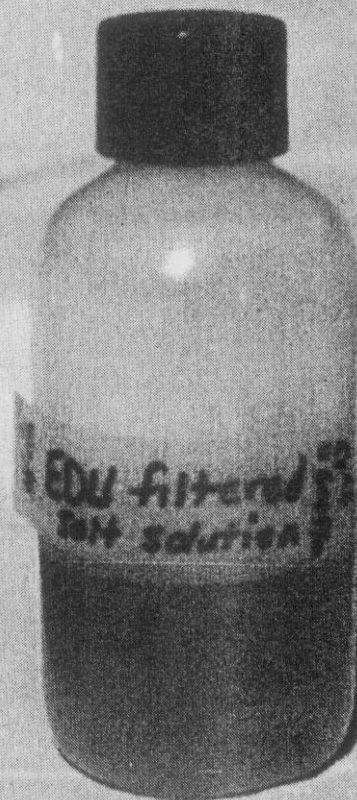
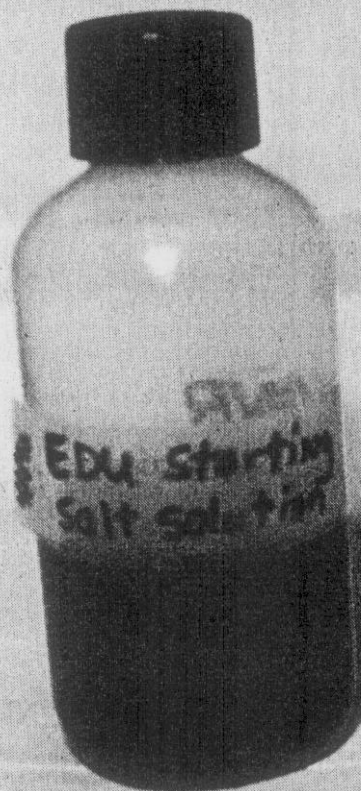


Figure 8

Table 6 indicates that chloride concentration in the solution is 120,000 ppm, or 94 wt% of sodium chloride in dry spent salt. Concentrations of soluble metal species, except Cr^{6+} , are very low due to their low solubilities in water.

Concentrations of several metal ions, e.g. $\text{Fe}^{2+}/\text{Fe}^{3+}$ and Ni^{2+} , decreased with settling time, an indication of possible slow kinetics of metal oxide formation. Sulfiding the solution with sodium hydrogen sulfide, NaSH , will enhance the removal efficiency of metal ions due to extremely low solubilities of metal sulfides in water and improved kinetics. More comprehensive sulfiding experiments, as well as measurements of metal ions concentration at different times, are needed before reaching a solid conclusion.

Table 6: Solution Analysis

Species	Concentrations, ppm				After Cr Removal *
	1 hr	22 hrs	40 hrs	64 hrs	
Cl^-	120,000				120,000
$\text{Fe}^{2+}/\text{Fe}^{3+}$	21.0	5.0	6.5		2.8
Ni^{2+}	45.0	9.7	9.5		2.0
Cr^{6+}	540.0	560.0	525.0		0.5
Mn^{2+}		17.4	17.5		20.6
SiO_2		340.0	350.0		60.0
SO_4^{2-}			200.0		2600.0
Cu^{2+}				6.4	0.5
Zn^{2+}				1.3	0.5
Mo^{6+}				131.0	46.0
PO_4^{3-}				5.5	0.5
NO_3^-				4.6	16.4
Solution No.	1	1	1	2	3

* Dithionite was added for Cr removal a week after dissolving the salt.

3. Filtration 1/Drying 1

The salt solution was then filtered with a Whatman 542 filter paper, which has an average pore size 2.7 microns. Filtration was slow, less than 0.3

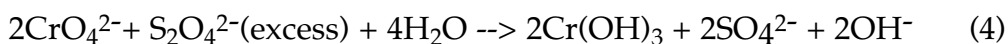
mL/min/cm², probably due to presence of spongy metal hydroxides/oxides. The wet solid, after drying (Solid 1, from Figure 4), was analyzed using XRF. Table 7 shows the results. As expected, solid 1 contains mostly oxides of metals such as Ni, Cr, Fe, Mn, Cu, etc., which are major alloying elements of Inconel and stainless steel, along with minor amounts of Na and Cl due to coprecipitation.

Table 7: Elemental Composition of Solids 1 & 2

Element	Compositions, wt%	
	Solid 1	Solid 2
Na	2.39	5.84
Al	0.23	0.02
Si	0.63	0.16
P	1.01	0.07
S	0.13	5.62
Cl	1.02	3.16
K	0.09	0
Ca	0.25	0.51
Ti	0.03	0
V	1.45	0.29
Cr	13.1	22.9
Mn	4.74	0.65
Fe	7.45	0.01
Co	0.12	0.01
Ni	13.4	0.16
Cu	5.67	0.26
Zn	0	0.06
Mo	0.34	0.52
W	0.37	0.21
Elements lighter than Na	47.68	59.55

4. Chromate Removal (Dithioniting)

The filtrate, solution 2, was light greenish-yellow in color (Fig 5, middle). Dithionite, Na₂S₂O₄, an effective reducing agent which works well in neutral and alkaline solution, was used and the reaction is shown as follows:



Chromium hydroxide, a green gelatin-like solid, precipitated as a result of the reaction. Excess dithionite is normally required to improve the conversion

efficiency. For the current experiment, 8X stoichiometry was used and the result was excellent, as shown in Table 6. Concentration of Cr^{6+} dropped to < 1 ppm from > 500 ppm. Table 6 also shows that sulfate ions in the solution, a benign species which should not be a concern, increased from 200 ppm to 2600 ppm after the dithioniting step. The result indicates that dithioniting is an excellent means to remove chromium from the solution.

5. Filtration 2/Drying 2 &3

The solution was then filtered to remove chromium hydroxide with a Whatman 542 filter paper. Filtration speed was measured at about 1 mL/min/cm², which was faster than that of Filtration 1. The filter cake was dried to Solid 2 at 100°C in an oven overnight and sent to Analytical Laboratory for XRF analysis. The composition of Solid 2 is also shown in Table 7. It indicates a high content of chromium in the solid, along with coprecipitants such as sodium chloride and sodium sulfate. Quantities of other metal species are small. Solid 1 and Solid 2 can be combined and sent for disposal. In the MWMF project [2], these solids may contain radionuclides, and would be encapsulated in a ceramic final form. Combined weight of Solid 1 and Solid 2 was only about 4.3 grams, about 1.1 wt% of the weight of spent salt initially dissolved. This is a significant reduction in the amount of toxic material for disposal.

The filtrate, Solution 3 (shown in Figure 5, right), was clean and can be dried to yield clean salt. Table 8 shows concentrations of species after the clean-up process, along with the Universal Treatment Standards (UTS) for allowable land disposable level without polymer encapsulation. It indicates that selenium (Se) is the only component exceeding the disposable limit. Concentration of Se in the solution was 0.9 ppm (or 4.5 ppm on a dry basis) which was slightly higher than the UTS disposable limit of 3.3 ppm.

Figure 6 shows the pictures of spent salt (far left), solid 1 (black, middle left), solid 2 (green, middle right), clean salt (far right) along with solutions 1, 2, and 3.

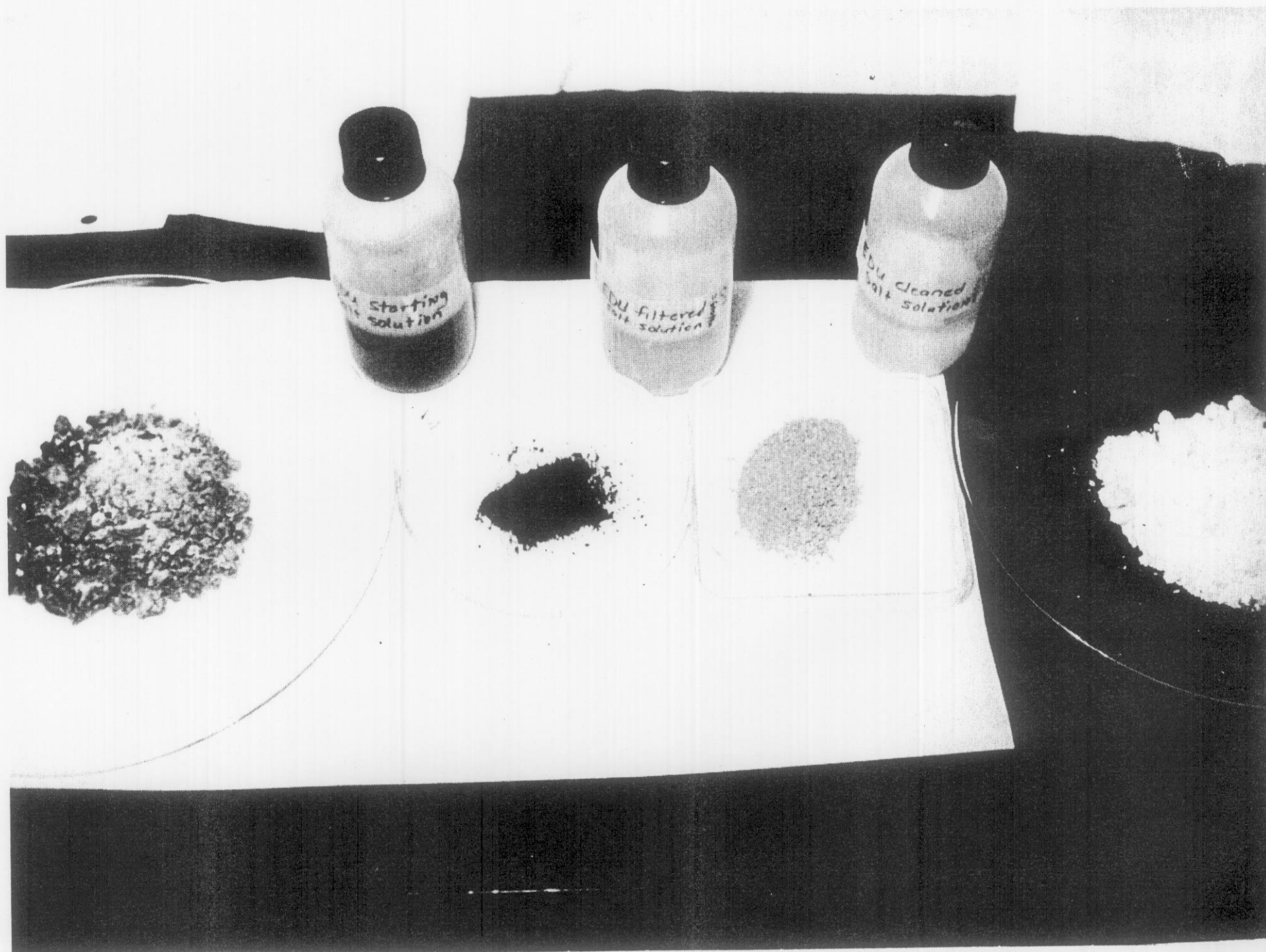


Figure 6

Table 8: Solution Analysis

<u>Species</u>	<u>In solution</u>	<u>Concentrations, ppm</u>	
		<u>Dry salt residue</u>	<u>UTS Limit</u>
Fe	2.8	13.9	NR
Ni	2.0	9.9	100.0
Mn	20.6	102.0	NR
Cu	0.5	2.5	250.0*
Zn	0.5	2.5	105.0
Cr**	0.5	2.5	16.5
Mo	46.0	228.0	3500.0*
As**	0.5	2.5	100.0
Se**	0.9	4.5	3.3
Ba**	0.04	0.2	152.0

Be,Cd,Pb,Ag,V,Co,Tl were undetectable by ICP/MS

* Per STL standard.

** measured by ICP/MS, total chromium was about 6 ppm due to small particles of chromium hydroxide, $\text{Cr}(\text{OH})_3$, which passed through the 2.7 micron filter. Use of finer pore-size of filter element should eliminate this problem.

Expedited MSO Demonstration with Salt Clean-Up System

Lawrence Livermore National Laboratory is in the process of building a pilot-scale MSO demonstration facility, to be completed in September 1997. It integrates MSO reactor with subsystems such as feed preparation, off-gas treating, spent salt clean-up, and final form encapsulation. Salt clean-up system, with capacity of processing 160 kg of spent salt for each run, is shown schematically in Figure 7. This system is designed based on the process developed in the laboratory.

Conclusions

We have developed a process to clean-up spent salt for MSO reactor. The process can treat various types of spent salt. We have demonstrated this process in the lab on a spent salt from EDU, which had a high chloride but low ash content. The results show that most metals precipitate out during the dissolution process. Further removal of metals, such as, chromium, can be accomplished in the dithioniting step. In the near future, the process will be demonstrated with other types of spent salt.

Acknowledgments

Funding was provided by EM-30 under the Mixed Waste Management Facility project.

References

1. "Spent Salt Clean-up/Recovery Process Development for Molten Salt Oxidation," Peter C. Hsu, Erica H. von Holtz, David L. Hipple, Leslie J. Summers, and William A. Brummond, a patent disclosure, LLNL, May 1996
2. "Mixed Waste Management Facility," UCRL-Prop-116761, L-17293-1, April 1994
3. "Design Parameters for Aqueous Processing of Melts from Molten Salt Destruction of Mixed Wastes," A. J. Darnell and R. L. Gay, MSDS-XY-0002, Energy Technology Engineering Center, Canoga Park, California, January 1991
4. "Development of Advanced Waste Treatment Technologies for demonstration in the Mixed Waste Management Facility," M. G. Adamson, Z. Chiba, E. H. von Holtz, and R. D. Streit, pages 4.1.1-4.1.15, Proceedings of the Third Biennial Symposium, Baltimore, Maryland, August 7-10, 1995
5. Private communications with John Bowers of LLNL, Nov., 1995
6. "EQ 3/6, A Software Package for Geochemical Modeling of Aqueous Systems," Thomas J. Wolery, UCRL-MA-11062, Sept. 1992
7. "Process Modeling of Salt Recycle with EQ 3/6", upcoming report by P. C. Hsu, D. A. Jones, D. L. Hipple, E. H. von Holtz, and Martyn Adamson
8. "Uranium Removal in the Spent Salt Cleanup Process for Molten Salt Oxidation," P.C. Hsu, L. Summer, E.H. von Holtz, D. Hipple, and Martyn Adamson, to be presented in the AIChE Spring National Meeting, Houston, March 1997
9. "Distributions of 14 Elements on 63 Absorbers from Three Simulant Solutions (Acid-Dissolved Sludge, Acidified Supernate, and Alkaline Supernate) for Hanford HLW Tank 102-SY," S. F. Marsh, Z. V. Svitra, and S. M. Bowen, LA-12654, Rev. 1, Los Alamos National laboratory, Los Alamos, NM, August 1994